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(54) A Method for the Catalytic Hydrogenation of Impure Maleic Acids

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Detailed Description of the Invention

This invention relates to a method for manufacturing one or more of  $\gamma$ -butyrolactone, 1,4-butanediol and tetrahydrofuran by hydrogenating impure maleic acids.

$\gamma$ -Butyrolactone is useful as a solvent for polyacrylonitriles, polymethacrylates and cellulose acetate, 1,4-butanediol is useful as a raw material of polyurethane and tetrahydrofuran is useful as a solvent of synthetic resins and of polyvinyl chloride in particular.

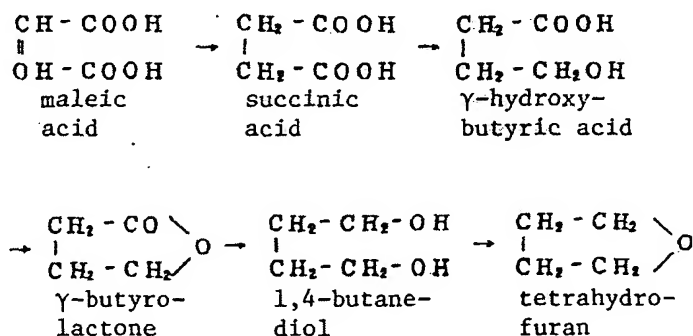
Various methods have been proposed for the catalytic hydrogenation of pure maleic acid or pure maleic anhydride. The attention of the inventors was drawn to the advantages, in the process of the manufacture of these acids, of performing hydrogenation using the raw materials in unaltered form without performing such pretreatments as purifying or esterifying impure products and perfected this invention by conducting repeated research.

Maleic acids are ordinarily manufactured by gaseous phase oxidation of benzene or C<sub>4</sub> hydrocarbons. The high temperature reaction gas is cooled and the crude maleic anhydride that is obtained is contaminated by quinone, complex oxidation by-products such as aldehydes and other impurities. Therefore, they are purified and pure maleic anhydride is obtained. When said reaction gas is introduced into flowing water, it is captured as an aqueous solution of maleic acid. This substance is present together with various oxidation by-products and other impurities and is slightly colored.

On the other hand, when phthalic anhydride is manufactured by gaseous phase oxidation of naphthalene or o-xylene, the maleic acid that is obtained as a by-product is discharged together with the waste gas. Said waste gas is usually washed with water and is captured as an aqueous solution of maleic acid. This substance also contains a very large quantity of impurities.

The objective of this invention is to manufacture one or more of  $\gamma$ -butyrolactone, 1,4-butanediol and tetrahydrofuran of high industrial value by direct hydrogenation as described above without performing such pretreatments as purification of impure maleic anhydride or aqueous solutions of impure maleic anhydride as described above.

It is well known conventionally that the products described above are obtained when aqueous solutions or organic solvent solutions of pure maleic acid are hydrogenated under increased pressure using a ruthenium or rhenium catalyst and it is presumed that the reaction takes the following course.



In this case, with ruthenium a high pressure of greater than 600 atmospheres is generally necessary and there is a high production volume of butanol and butyric acid, which are of comparatively low value. Although this is not undesirable, on the other hand, in the case of rhenium catalyst, when the pressure is greater than 200 atmospheres, the reaction proceeds well and more than 85% of the maleic acid is utilized in the production of the aforementioned useful substances under suitable conditions, with only a small quantity of butanol and succinic acid being obtained as by-products. The proportions of these three products can be varied as desired by selection of the reaction conditions.

However, when aqueous solutions of impure maleic acid are hydrogenated directly in the presence of a known rhenium catalyst, the reaction speed is slowed, the reaction is held at the  $\gamma$ -hydroxybutyric acid or  $\gamma$ -butyrolactone stage and does not tend to progress beyond that stage. When the temperature is increased in order to accelerate the reaction speed, a large quantity of butanol and butyric acid is produced as by-products and high yields as in the case of pure maleic acid cannot be obtained. The cause of this is presumed to be that the activity of the catalyst is lost due to the impurities that are also present. However, the details are not clear.

In this invention, the first stage of hydrogenation in the hydrogenation of impure maleic acids is performed using a catalyst of which the principal component is a platinum group element. After the harmful impurities in the aforementioned rhenium catalyst have been rendered harmless, the platinum group catalyst is removed and the second stage of hydrogenation is performed using a catalyst of which rhenium is the principal component. By this means, success is achieved in obtaining good yields in any desired proportions of the aforementioned three products.

In this invention, the impure maleic acid aqueous solutions are used in the form of aqueous solutions, impure maleic anhydride or organic solvent solutions, or, when water is added, in the form of maleic acid aqueous solutions. Organic solvents that can be used include, for example, lower alcohols and saturated hydrocarbons.

Any platinum group catalyst can be used as the first stage hydrogenation catalyst in this invention. However, platinum, palladium, ruthenium and rhodium are particularly desirable. When two or more of the aforementioned metals are used, they may be used in unaltered form or as alloys. In addition, a small quantity of a component that promotes catalytic action such as, for example, oxides of barium, calcium and magnesium can be compounded with this catalyst. They can also be used carried on porous, inactive substances such as, for example, alumina, silica, charcoal, pumice and celite.

The rhenium catalyst that is used as the second stage hydrogenation catalyst of this invention may be rhenium oxide or catalysts of which the principal component is rhenium obtained from other rhenium compounds, and, in particular, may be rhenium black obtained by reducing rhenium oxide. Further, in order to intensify catalytic action, a method in which small quantities of other components are admixed and ordinary

methods in which the rhenium is carried, for example, on alumina, silica, charcoal, pumice and celite can be used.

The quantity of catalyst in the first stage hydrogenation should be 0.1 to 1.0 g, and, preferably, 0.2 to 0.8 g, per 1 mol of raw materials. The pressure should be greater than 50 atmospheres, and, preferably, 100 to 250 atmospheres. The temperature should be 50 to 200°C, and, preferably, 80 to 130°C. The reaction time should be less than 1 hour, and, preferably, 0.5 to 1 hour.

The quantity of catalyst in the second stage hydrogenation should be 0.5 to 3 g, and, preferably, 1 to 2 g, per 1 mol of raw materials. The pressure should be greater than 200 atmospheres, and, preferably, 250 to 300 atmospheres. The temperature should be 150 to 500°C, and, preferably, 200 to 250°C. The reaction time should be 0.5 to 5 hours, and, preferably, 2 to 4 hours.

When the quantity of catalyst is below the lower limit of the aforementioned range, the reaction does not proceed sufficiently and the target substance cannot be obtained in high yields. Although the reaction rate is accelerated as the amount used is increased, at amounts above the upper limit its use is not economical.

When temperature and pressure are below the lower limits of the aforementioned ranges, the target substances cannot be obtained in high yields. Although it is preferable for them to be on the high side, when they are above the upper limits, the reaction proceeds to an excessive degree and there are increases in products such as butanol. Reaction time can be determined as desired within the range described above depending on the combination of quantity of catalyst, temperature and pressure. When it is below the lower limit, the reaction is not sufficiently completed. When it is above the upper limit, butanol and other substances are produced as by-products and the yields of the target substances are decreased.

After the second stage reaction has been completed, the catalyst is removed, the three target substances are separated by standard methods, and, as required, are purified. For example, the reaction solution can be distilled at normal pressure or under reduced pressure to separate the tetrahydrofuran,  $\gamma$ -butyrolactone and butanol are extracted with ether from this distillation residue, the ether and butanol are removed from the extraction solution and  $\gamma$ -butyrolactone is obtained. When necessary, it can be purified by distillation. The extraction residues from the ether extraction is distilled and 1,4-butanediol is obtained.

This invention can, of course, be applied to pure maleic acid and pure maleic anhydride. However, it can also be applied to pure crystals and impure crystals of fumaric acid, which is an isomer of maleic acid.

Further, this invention can be executed by either the batch method or the continuous method.

### Example 1

A reaction gas containing maleic anhydride that was obtained by gaseous phase oxidation of benzene was washed with water and 50 cc of the aqueous solution dark brown impure maleic acid (containing 23.64 g of maleic acid) that was obtained and 0.15 g of platinum black were introduced into a 100 cc autoclave manufactured of an acid-resistant material and the mixture was heated for 50 minutes at 110°C and at a hydrogen pressure of 100 atmospheres. The product was colorless and transparent and no unsaturated compounds were found. The platinum black catalyst was removed from the contents by filtration, 0.2 g of rhenium chloride was added to this reaction solution and it was heated in the aforementioned reaction container for 4 hours at 200 to 210°C and at a hydrogen pressure of 290 atmospheres. The product did not exhibit acidity and its composition was as shown below.

$\gamma$ -Butyrolactone	2.0 g	
1,4-Butanediol	4.3 g	} Yield for maleic acid of 68.1% (Excluding the yield of methanol. The same applies below)
Tetrahydrofuran	4.9 g	
Butanol	0.7 g	

### Example 2

The same procedure was performed as in Example 1 except that a material comprised of 0.15 g of palladium black carried in 20 g of charcoal was used instead of platinum black as the first stage catalyst in Example 1, that the temperature was set to 130°C and that a material comprised of 0.2 g of rhenium black carried on 4 g of charcoal was used instead of rhenium black only as the second stage catalyst. A product of the composition indicated below was obtained.

$\gamma$ -Butyrolactone	1.98 g	
1,4-Butanediol	4.0 g	} Yield for maleic acid of 68.1%
Tetrahydrofuran	5.2 g	
Butanol	0.8 g	

### Example 3

The waste gas obtained when phthalic anhydride was manufactured by gaseous phase air oxidation of o-xylene was washed with water, a 50 cc aqueous solution of dark brown impure maleic acid (containing 23.64 g of maleic acid) that was collected and 0.1

g of ruthenium black were introduced into the same type of reaction container as in Example 1 and the mixture was heated for 1 hour at 100°C at a hydrogen pressure of 150 atmospheres, after which the catalyst was removed by filtering the contents. This reaction solution and 0.2 g of rhenium black were introduced into the reaction container described above and the mixture was heated for 3 hours at 230 to 240°C at a hydrogen pressure of 260 atmospheres. The product did not exhibit acidity and its composition was as follows.

$\gamma$ -Butyrolactone	4.2 g	
1,4-Butanediol	4.0 g	} Yield for maleic acid of 82.5%
Tetrahydrofuran	5.4 g	
Butanol	0.8 g	

#### Example 4

A product having the composition indicated below was obtained by the same procedure as in Example 3 except that a catalyst obtained by mixing 0.005 g of rhodium black instead of the ruthenium black and 0.05 g of platinum black carried on 2 g of [illegible] was used instead of the first stage catalyst in Example 3.

$\gamma$ -Butyrolactone	4.1 g	
1,4-Butanediol	4.2 g	} Yield for maleic acid of 81.6%
Tetrahydrofuran	5.2 g	
Butanol	0.7 g	

#### Example 5

A product having the composition indicated below was obtained by exactly the same procedure as in Example 3 except that a substance consisting of 20 g of crude maleic anhydride obtained by gaseous phase oxidation of benzene dissolved in 50 cc of methanol was used and that 0.1 g of rhodium black was used in the first stage.

$\gamma$ -Butyrolactone	4.3 g	
1,4-Butanediol	4.3 g	} Yield for maleic acid of 84.0%
Tetrahydrofuran	5.2 g	
Butanol	0.8 g	

## Comparative Example 1

The waste gas obtained when phthalic anhydride was manufactured by gaseous phase air oxidation of o-xylene was washed with water, the aqueous solution of impure maleic acid (containing 11.2 g of maleic acid) that was collected and 0.1 g of rhenium black were introduced into the reaction container of Example 1 and the mixture was heated for 4 hour at 230 to 240°C at a hydrogen pressure of 280 atmospheres, after which carboxylic acid groups corresponding to 34.9% of the maleic acid used remained in the product. Its composition is shown below.

$\gamma$ -Butyrolactone	3.1 g	
1,4-Butanediol	0.5 g	} Yield for maleic acid of 56.2%
Tetrahydrofuran	0.9 g	
Butanol	0.2 g	

## (57) Claim

1. A method for manufacturing one or more of  $\gamma$ -butyrolactone, 1,4-butanediol and tetrahydrofuran characterized in that, in the first stage, impure maleic acid or impure maleic anhydride is hydrogenated in the presence of a catalyst of which a platinum group element is the principal component, after which said platinum group catalyst is removed from said reactants, and, in that, in a second stage, further hydrogenation is performed in the presence of a catalyst of which rhenium is the principal component.

## (56) References

Reduction of oxidation of organic compounds, Y. Ogata, 1 November 1963, p. 567, Example 1. Publisher: Nankodo

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